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None

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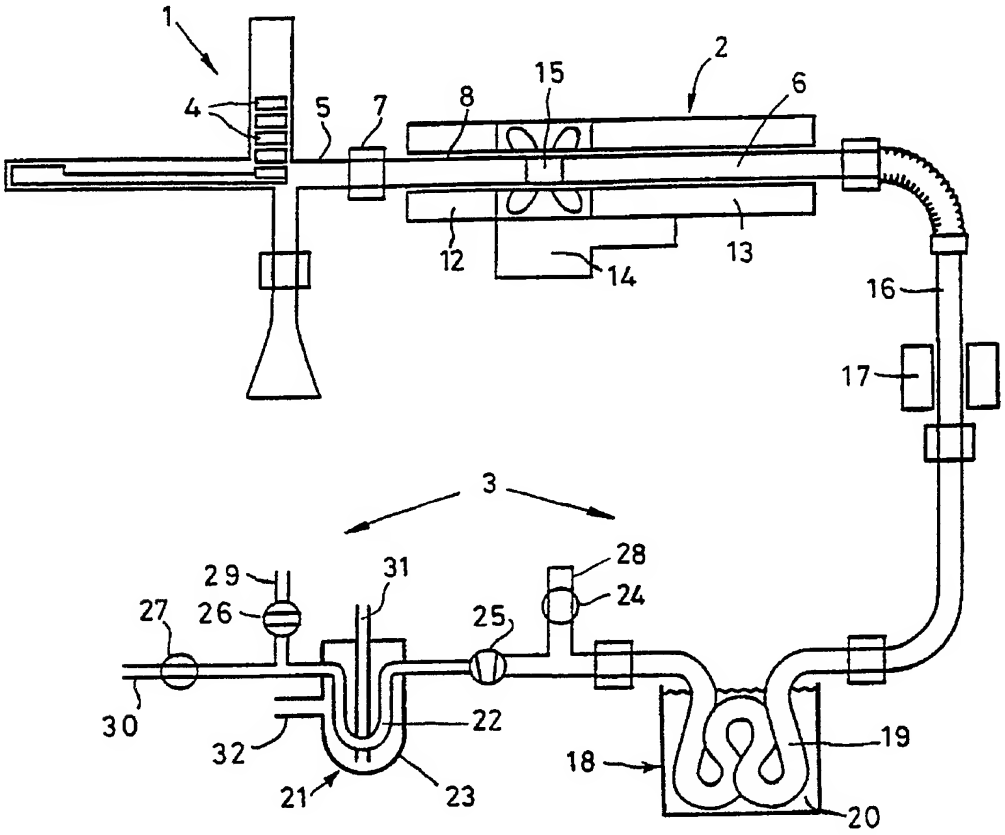
(54) Analysing materials with hydrocarbon potential

(57) Apparatus for analysis of materials (4) e.g. rock or kerogen with hydrocarbon potential has a pyrolysis furnace assembly (2) for combustion and oxidation of material to CO_2, cold traps (20, 21) to remove CO_2 and a mass spectrometer to analyse gases for CO_2 after release from the traps. A furnace assembly with three independently controlled heating windings is further disclosed.

FIG.1.



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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

FIG.1.

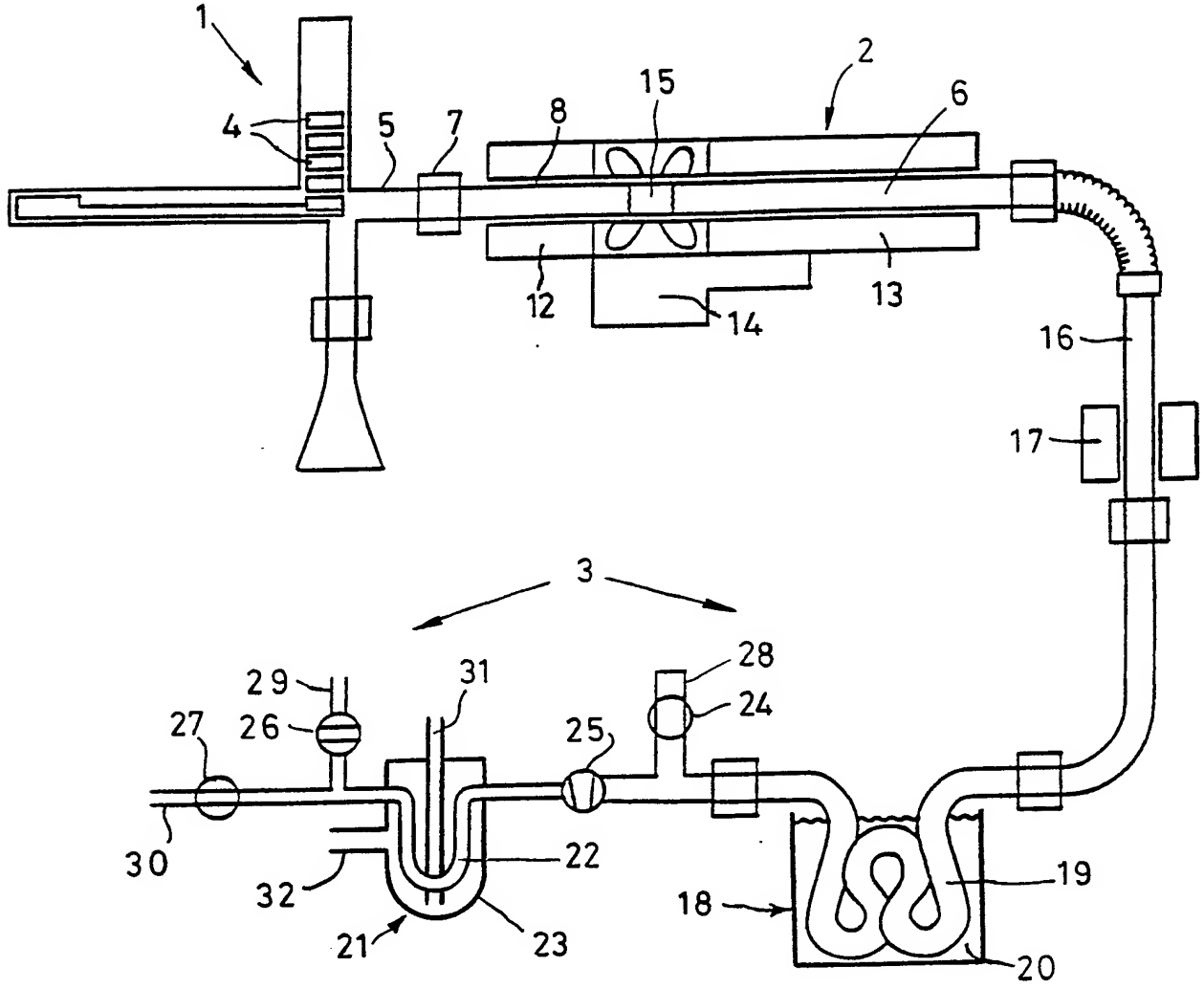
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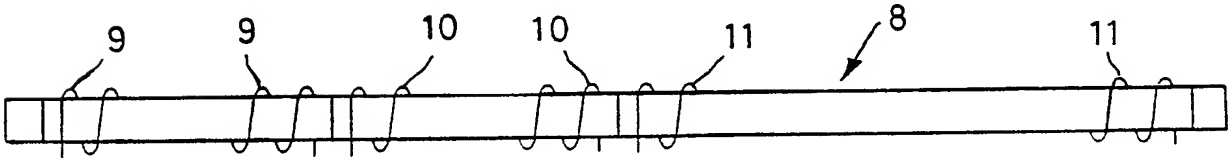
FIG.2.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APPARATUS FOR ANALYSING MATERIAL HAVING A HYDROCARBON POTENTIAL

This invention relates to apparatus for analysing material having a hydrocarbon potential and is particularly useful in apparatus for effecting automated pyrolysate isotope procedures.

The apparatus may be designed to achieve automated batchwise analysis of the stable carbon isotope ratios of pyrolysate evolved from precursor kerogen/rock powders.

Such analyses have been performed previously, but only under manual conditions. It is therefore one object of the present invention to provide procedures that enable automation to take place by the use of hardware and software designed to operate according to a predetermined timing sequence.

According to one aspect of the present invention, apparatus for analysing material having a hydrocarbon potential comprises means for introducing a batch of the material into a furnace for pyrolysis, means for subsequently oxidising the products of the pyrolysis by combustion to CO_2, collecting the CO_2 cryogenically and analysing the collected material as a gas on a mass spectrometer.

According to another aspect of the present invention a furnace assembly for use in the aforesaid apparatus comprises a rigid tube, three independently controllable heating windings wound on the tube in series therealong, heat insulating material applied externally to the first and third windings and a cooling blower mounted for cooling the second winding whereby a batch of material can be subjected to pyrolysis within the first winding with the pyrolysate trapped within the cooled winding with light products passing through the third winding to vent and the trapped pyrolysate can subsequently be remobilised by heating the second winding to be passed for combustion in the third winding and

discharged therefrom for test. By winding the three heating windings on a single tube cold spots can be eliminated.

According to yet a further aspect of the invention, an automated pyrolysate isotope method of analysis comprises using a first furnace to heat a batch of material having a hydrocarbon potential in a gaseous carrier stream to produce a pyrolysate, trapping said pyrolysate in a second furnace while being cooled by a blower and the light products of the pyrolysate are passed to vent, heating the second furnace to remobilise the trapped pyrolysate to pass through a third furnace for combustion to CO_2 and water, passing this CO_2 and water in the carrier gas through a water trap and then the CO_2 and carrier gas through a liquid nitrogen trap to freeze the CO_2 and enable the carrier gas to pass to vent, pumping out remaining carrier gas before heating the liquid nitrogen trap to convert the frozen CO_2 to gaseous form, and passing the converted CO_2 to a mass spectrometer.

In order that the invention may be clearly understood and readily carried into effect apparatus for an automated pyrolysate isotope procedure will now be described in some detail, by way of example, with reference to the accompanying drawings, in which:-

Figure 1 is a diagrammatic representation of a major portion of the apparatus; and

Figure 2 is a diagram of an element in the portion represented in Figure 1.

The apparatus comprises four main components, namely a sample introduction module 1, furnace assemblies 2, a purification/collection assembly 3 and a mass spectrometer (not shown).

The sample introduction module is described in the specification of patent application No. 9219028.9 and is arranged for capsules 4, each containing a substance to

be treated, to be delivered through a tube 5 to a 650mm length of 12mm outside diameter silica tubing 6 connected to the tube 5 by a Cajon "Ultra-Torr" compression fitting 7 with a bore of 12.7mm. The silica tubing 6 is contained in a 14mm inside diameter ceramic tube 8 (Fig.2) which carries three separately controlled furnaces wound on the single tube in series and consisting of a winding 9 for pyrolysis, a winding 10 for remobilisation of trapped pyrolysate and a winding 11 for combustion of volatilised pyrolysate. The pyrolysate and combustion windings 9, 11 are fully insulated by means 12, 13 but the intermediate winding is open to cooling by a centrifugal blower 14. In use the pyrolysis section of the tube is maintained so that the actual temperature of the sample capsule 4 attains 550°C (635°C as detected by a thermocouple). The remobilisation section of the tube is maintained at a temperature selected between approximately 30°C and 350°C. The combustion section of the tube is maintained at 900°C.

A wad of silica wool is positioned in the silica tubing 6 so that it lies centrally with respect to the remobilisation winding 10. Cupric oxide (wire form) fills the distal end of the silica tubing so that it occupies the length of the combustion winding 11.

Attached to the distal end of the silica tubing 6 is a separate 260mm length of silica tubing 16 which is vertically mounted. The top 100mm of this tubing is filled with MnO_2 while the bottom 60mm is filled with platinum coated silica (Leco catalyst pellets product code: 501-587). This catalyst is maintained at a temperature of around 400°C by a small furnace 17 (Leco product code: 507-200).

Referring now to the purification/collection assembly 3 this includes a first trap 18 comprising a 609.6mm long 6.35mm flexible tube 19 connected to receive the output from the silica tubing 16 and folded for

immersion in propanol 20 when cooled to less than -50°C.

A second trap 21 connected in series with the first trap 18 comprises a U-shaped length of 3.2mm stainless steel tubing 22. This is surrounded by a sealed stainless steel jacket 23 providing a space into which liquid nitrogen may be pumped for cooling the tubing 22. The stainless steel jacket 23 is also wound with heating cord so that the trap may alternatively be heated. The arrangement is also provided with valves 24, 25, 26, 27 and vents 28, 29 so that the flow of gas may be vented before or after the second trap 21 and the second trap 21 may be isolated from the proximal part of the system by the valve 25.

The purification/collection system 3 is directly connected at 30 to the inlet valve of a dual inlet, double collector, gas source, stable isotope mass spectrometer. This is controlled automatically by an Amiga 2000 data system that can be modified to control the entire system. The various connections in the assemblies described above are effected by appropriate compression fittings and flexible or standard stainless steel tubing of different diameters.

In practice, operation of the automated pyrolysate isotope procedure involves loading the sample capsules into the introduction module 1, entering the sample identification into the data system and starting the run. The system may also be operated manually using the Amiga data system, if required. Seven stages during one cycle of operation are broadly indicated below with reference to Figure 1.

1. In standby, helium introduced under pressure into the sample introduction module 1 is passed through the system to act as a purging agent to the helium being vented through the vent 28 after passing through the propanol trap 18. The liquid nitrogen trap 21 is maintained under vacuum through the connection 30 with

the mass spectrometer, the valve 25 being closed. The cooling blower 14 for the remobilisation furnace (winding 10) remains in operation.

2. The liquid nitrogen trap 21 is isolated from the mass spectrometer by the valve 27 and liquid nitrogen from a dewar is drawn in through a pipe 31 by the actions of a pump through a connection 32.

3. When the liquid nitrogen trap 21 has attained a temperature of less than -150^{o} (in this particular example) a sample capsule 4 is inserted into the pyrolysis furnace (winding 9). At $550^{o}C$ pyrolysis takes place and the evolved pyrolysate is trapped adjacent to the silica wool plug 15 in the cooled remobilisation action furnace. Light products of pyrolysis (C_1 to about C_8) pass through the combustion furnace (winding 11) to be converted to CO_2 and vented through the vent 28.

4. After five minutes, the sample capsule is withdrawn and the trapped pyrolysate is remobilised by heating the remobilisation winding 10 with the blower 14 stopped. The vent 28 is closed the valve 25 opened and the vent 29 opened. The remobilised pyrolysate is swept by the helium carrier through the cupric oxide in the combustion furnace (winding 11) at $900^{o}C$ and is oxidised to CO_2 and water. The water is trapped by the propanol trap 18, the CO_2 is trapped by the liquid nitrogen trap 21 and the helium is vented through the vent 29.

5. After ten minutes the vent 29 is closed by the valve 26 and valve 25 is closed. The valve 27 is opened to connect the liquid nitrogen trap 21 to vacuum to enable the helium to be withdrawn while the CO_2 remains frozen. The furnace blower 14 is activated.

6. When the vacuum condition returns to the liquid nitrogen trap 21, the valve 27 is closed to isolate this trap from the mass spectrometer, the liquid nitrogen pump is turned off and the heating cord surrounding the jacket 23 of the trap 21 is activated for 30 seconds to bring

the CO_2 up to room temperature.

7. The valve 27 is opened to admit the CO_2 to the mass spectrometer and allowed to equilibrate before the valve 27 is again closed. The gas is then automatically analysed by the mass spectrometer and the results displayed, dumped to a printer and stored on disk.

Crucial to the effectiveness of the system are the flow rate of the helium carrier gas and the timing of the period of pyrolysis/venting. The optimum carrier gas flow rate has been determined at 18-20cc min. The optimum period for pyrolysis/venting is 5 min. Shorter than this and pyrolysis is incomplete; longer and the helium starts stripping the lighter ends off the evolved pyrolysate.

The apparatus for automated pyrolysate isotope procedure described above has been used to analyse the pyrolysate derived from kerogen and pre-extracted rock powders. As a consequence of the linear relationship between the major beam pressure (as measured by the mass spectrometer at a set volume) and the volume of CO_2, the system may also be used to determine the S_2 value of the kerogen, providing the initial sample weight is known. The system can also be used to analyse any other material with hydrocarbon potential. Simple modification of the apparatus and software would also enable the analysis of the C_1 to C_8 fraction derived from pyrolysis, or allow the system to be used for the analysis of whole oils, total extracts and fractions.

CLAIMS:

1. Apparatus for analysing material having a hydrocarbon potential comprising means for introducing a batch of the material into a furnace for pyrolysis, means for subsequently oxidising the products of the pyrolysis by combustion to CO_2, collecting the CO_2 cryogenically and analysing the collected material as a gas on a mass spectrometer.

2. Apparatus according to claim 1, in which the furnace for pyrolysis is followed in sequence by a furnace for the remobilisation of trapped pyrolysate derived from the pyrolysis furnace and a combustion furnace for the combustion of volatilised pyrolysate, means being provided for enabling a carrier gas to carry the gaseous products of the pyrolysis to the means for collecting the CO_2 cryogenically and a blower being provided for cooling the remobilisation furnace while products of the pyrolysis are trapped therein.

3. Apparatus according to claim 2, in which the three said furances comprise respectively three electrical heating windings about a single support tube arranged to receive and convey the material for pyrolysis, the pyrolysate and gaseous products as well as the carrier gas passing therethrough.

4. Apparatus according to Claim 3, in which a wad is mounted in the support tube in register with the remobilisation furnace for arresting solid pyrolysate prior to its remobilisation.

5. Appartus according to claim 3 or claim 4, in which the support tube comprises a ceramic tube supporting the three windings and a concentric silica tubing for receiving and conveying the material for pyrolysis, the pyrolysate, gaseous products and carrier gas.

6. Apparatus according to any one of the preceding claims, in which the means for collecting the CO_2 cryogenically comprises a liquid nitrogen trap arranged

for the CO_2 to be carried thereinto by carrier gas for the CO_2 to be frozen in the trap, a vent being provided beyond the trap for the discharge of the carrier gas.

7. Apparatus according to claim 6, in which the liquid nitrogen trap is provided with means heating the frozen CO_2 to the gaseous form and delivering that gas to the mass spectrometer.

8. Apparatus according to any one of the preceding claims, provided with a water trap for removing any water in the CO_2 delivered from the combustion means, the water trap comprising a folded tubing arranged for the CO_2 to pass therethrough, the folded tubing being immersed in propanol.

9. A furnace assembly for use in apparatus according to any one of the preceding claims, comprising a rigid tube, three independently controllable heating windings wound on the tube in series therealong, heat insulating material applied externally to the first and third windings and a cooling blower mounted for cooling the second winding whereby a batch of material can be subjected to pyrolysis within the first winding with the pyrolysate trapped within the cooled winding with light products passing through the third winding to vent and the trapped pyrolysate can subsequently be remobilised by heating the second winding to be passed for combustion in the third winding and discharged therefrom for test.

10. Apparatus for analysing material having a hydrocarbon potential substantially as hereinbefore described with reference to the accompanying drawings.

11. An automated pyrolysate isotope method of analysis comprising using a first furnace to heat a batch of material having a hydrocarbon potential in a gaseous carrier stream to produce a pyrolysate, trapping said pyrolysate in a second furnace while being cooled by a blower and the light products of the pyrolysis are passed to vent, heating the second furnace to remobilise the

trapped pyrolysate to pass through a third furnace for combustion to CO_2 and water, passing this CO_2 and water in the carrier gas through a water trap and then the CO_2 and carrier gas through a liquid nitrogen trap to freeze the CO_2 and enable the carrier gas to pass to vent, pumping out remaining carrier gas before heating the liquid nitrogen trap to convert the frozen CO_2 to gaseous form, and passing the converted CO_2 to a mass spectrometer.

12. Each and every novel feature or novel combination of features herein disclosed.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number

GB 9220926.1

Relevant Technical fields

(i) UK Cl (Edition K) G1B (BCC)

(ii) Int Cl (Edition 5) G01N

Search Examiner

M R WENDT

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI, CLAIMS

Date of Search

10 NOVEMBER 1992

Documents considered relevant following a search in respect of claims 1-8, 10 AND 11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Category	Identity of document and relevant passages — 11 —	Releva to clain. s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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P: Document published on or after the declared priority date but before the filing date of the present application.

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